Study on the Magnetic Property of Artificial Magnetite and its related Phenomena

Study on the Magnetic Property of Artificial Magnetite and its related Phenomena

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Magnetism of semiconductor, being different from ferromagnetic metal, has a peculiarity in that the intensity of magnetization decreases abruptly at a low temperature[1]. Among the ferromagnetic semiconductors the magnetite, being composed of ferrous and ferric ions, has a magnetic transformation in the neighbourhood of −150°C and its magnetism is reduced by some amount.

This phenomenon could be explained in outline by the approximation applied either on Wilson model[2], or recently on Heitler-London model[3]. But there are very few experimental studies to decide upon the energy level of electrons in magnetite, so that it is desirous to perform on such line.

Hitherto, it has been considered that magnetite, like Fe_2O_3, CuO and so on, is no structure-sensitive semiconductor which has the impurity level. (Although any change in electric conductivity could not be expected by the heat treatment of the natural magnetite the existence of an excess of oxygen comparatively stable is an appropriate idea, we may think). Having a concern about this point, we will prepare the artificial magnetite with various methods and study the energy level of its electrons according to the conditions of preparation.

The artificial magnetite obtained by wet method. Magnetite is formed artificially by the following chemical reaction:

$$\left.\begin{array}{l} Fe^{++}+2OH^-\rightarrow Fe(OH)_2 \\ 2Fe^{+++}+6OH^-\rightarrow 2Fe(OH)_3 \end{array}\right\rangle FeO.Fe_2O_3.xH_2O$$

As shown in Fig. 1, OH^- solution in a flask A is boiled in vacuum by aspirator B, being prevented from oxidation and at the same time stirred sufficiently during the reaction. The mixed solution of ferrous and ferric salts with appropriate proportion in a fractional funnel C is slowly added to the OH^- solution and then a black precipitate is formed in the flask. More ferrous salt is necessary than the proportion so as to furnish $FeO\cdot Fe_2O_3$, because ferrous salt is oxidized during this procedure. The precipitate is washed by water and dried in vacuum. The results of chemical analysis show that the product is a mixed compound of hydrated $FeO\cdot Fe_2O_3$ and a small amount of Fe_2O_3. It is noteworthy that while in this process FeO itself can't be formed, $2FeO\cdot Fe_2O_3$ is precipitated and then readily oxidized into Fe_2O_3 by an excess of ferrous ion. The density of the artificial magnetite by wet method is 3.8, while that of the natural magnetite is 5.5. By heat treatment at 800°C the crystal water in the product can be taken off completely.

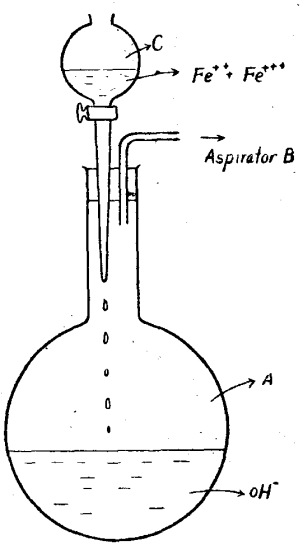


Fig. 1.

I. Difference of magnetizing Curve by various Heat Treatment

The artificial magnetite prepared by wet

method shows the almost indistinguishable diffraction ring from the natural magnetite in the X-ray photograph, but it will not be estimated as perfect magnetite because of hydrated and easily oxidized properties, etc., If we discuss the product as magnetite, heat treatment at high temperature is necessary.

From this point of view, after the artificial magnetite is heated at a pressure 6 mm Hg. or 5×10^{-3} mm Hg. at 900°C for two hours, the magnetizing curve of these samples was observed by the ballistic method, the result being shown in Fig. 2.

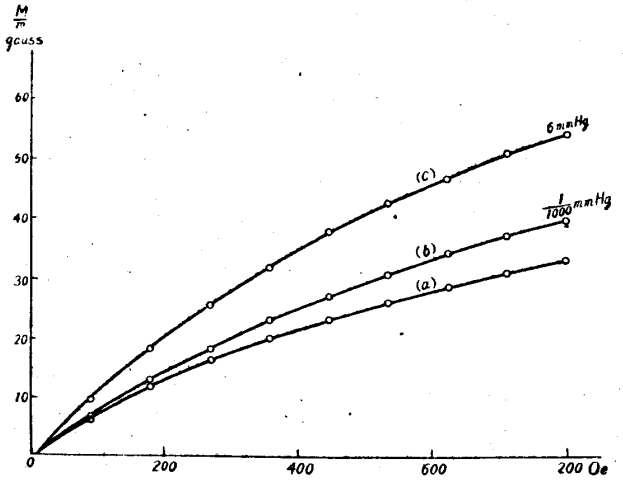


Fig. 2.

The ordinate represents the magnetic moment per unit mass and the abscissa the temperature. In this figure sample (a), without heat treatment, is dried in vacuum at 100°C. Comparing intensity of magnetization in the external magnetic field of 800 o_e, the value in sample (b) is increased from 28 gauss in sample (a) to 40 gauss by heat treatment at a pressure 10^{-3} mm Hg. at 900°C. This increase is probably due to the dehydration from the hydrated magnetite. But it is interesting that intensity of magnetization increases to 54 gaugg by heat treatment at a pressure 6 mm Hg. at 900°C in sample (c).

The results of chemical analysis show, sample (c) is oxidized and so more deviated from the composition of magnetite than sample (b). But the intensity of magnetization is less in sample (b) than in (c). Regarding this matter, we will study in future.

The existence of magnetic transformation

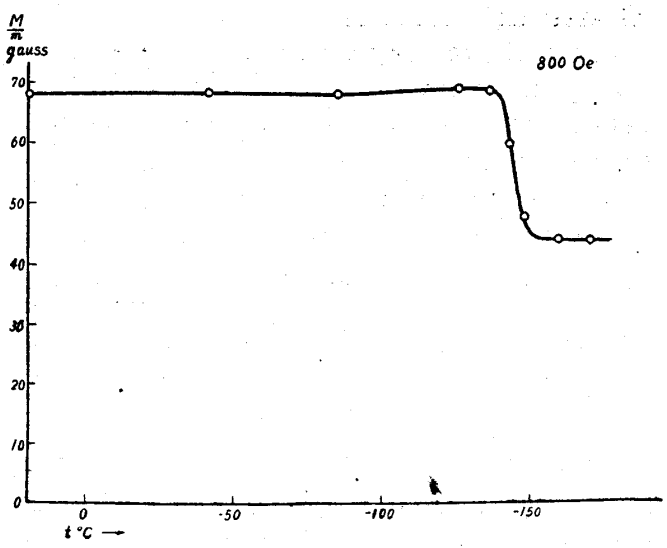


Fig. 3.

in the artificial magnetite. Fig. 3 shows the change of magnetization of the natural magnetite at Kamaishi iron mine due to temperature in the external field 800 o_e. In this figure, the ordinate represents magnetic moment per unit mass the abscissa the temperature. It is seen, that intensity of magnetization abruptly decreases at about −150°C. Can we expect the same change also in the artificial magnetite? Sample (a) and (b) have no magnetic transformation as shown in Fig. 4. The former is

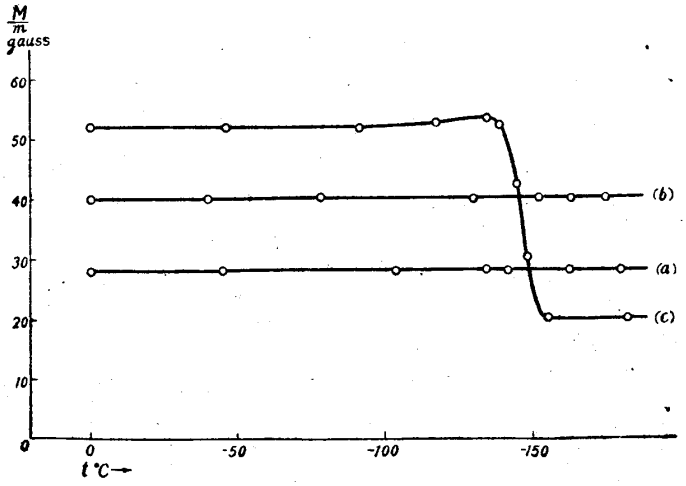


Fig. 4.

dried by heating at 100°C in vacuum and the latter treated at a pressure 5×10^{-3} mm Hg. at 900°C for 2 hours. But the transformation occurs as in the natural magnetite at −150°C in the sample (c), which is treated at a pressure 6 mm Hg. at 900°C for 2 hours. From these results, it is comprehensible that differences of magnetization in the artificial magnetite depend upon

its essential structure.

The artificial magnetite by oxydation at high temperature. It is imaginable that magnetite was formed in nature, when iron erupted upon the surface of the earth, had combined with oxygen in the air at high temperature. Now a preparation was tried applying the following chemical reaction, in order to obtain the artificial magnetite by the process analogous to the natural one $FeC_2O_4 \rightarrow FeO + CO_2 + CO \xrightarrow{O_2} FeO \cdot Fe_2O_3$. After ferrous oxalate has decomposed into ferrous oxide by heating in vacuum at 900°C, if slow oxidation proceeds in the vacuum lowered, $FeO \cdot Fe_2O_3$ is formed, for $F_2O \cdot Fe_2O_3$ is more stable than FeO at high temperature. The vacuum range is 10—760 mm Hg. while the oxidation goes on. To be observable is that,w hen FeC_2O_4 is being decomposed into FeO, the following oxidation, $FeO \rightarrow Fe_2O_3$, proceeds and $FeO \cdot Fe_2O_3$ cannot be produced, unless the vacuum is maintained as high as possible. The reason will be illustrated in such a way that ferrous oxide is very active while the reaction, $FeC_2O_4 \rightarrow FeO$, proceeds and the reaction temperature is comparatively low. Fig. 5 shows the

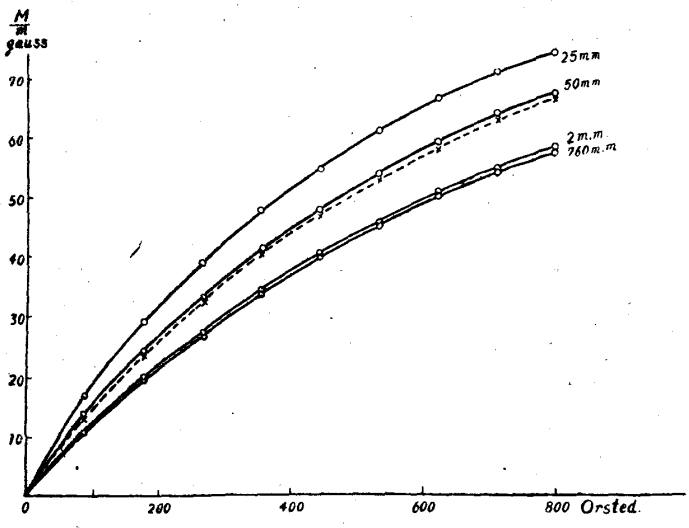


Fig. 5.

magnetizing curve of magnetites heated for 5 hours at 900°C at 20, 250, 500 and 760 mm Hg. respectively. In this figure the ordinate represents the magnetic moment per unit mass and abscissa the external field. Dotted curve shows the natural magnetite from Kamaishi. By this oxidation process at high temperature, the artificial magnetite which is stronger magnetic than the natural one can be formed. We may think for illustration the product has less impurity than the natural magnetite. As shown in Fig. 6, this artificial magnetite

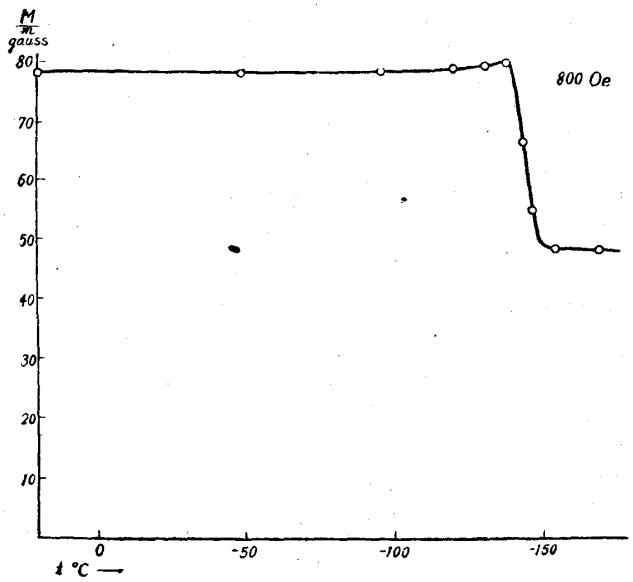


Fig. 6.

has magnetic transformation at −150°C. When we consider the existence of magnetic transformation in the artificial magnetite obtained by wet method according to the conditions of heat treatment, and also the magnetite produced by oxidation method at high temperature, the electronic structure of magnetite can be sensitively effected by the state of oxygen ion in crystal as that of the some other oxide semiconductors and the existence of transformation can be ascribed to the state of this oxygen ion. It seems appropriate to pay attention to oxygen ion, if we take into consideration that the artificial magnetite consists of comparatively pure iron ion, while the natural magnetite contains some impurities like sulphur, silica, titan, etc..

II. Conductivity of the artificial Magnetite

Will the increasing of intensity of magnetization in the artificial magnetite according to the conditions of heat treatment accompany the increasing of conductivity or not? Will be there the kink of the curve of electric conductivity which corresponds to magnetic transformation? We describe on these problems as follows:

For the measurement of conductivity as

a function of temperature, the samples are pressed into cylindrical form, each having 10 mm in diameter 5 mm in length. These samples are the magnetite prepared by wet method. Fig. 7 shows the apparatus of the

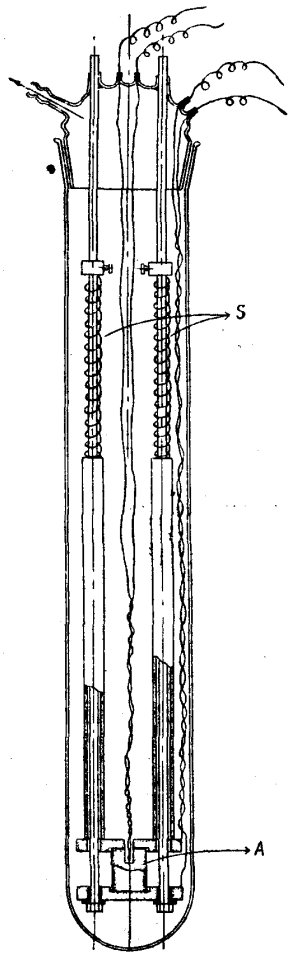


Fig. 7.

measurement of electrical conductivity. Spirals (s) are settled in order to contact the sample (A) with electrode satisfactorily. Temperature is observed by means of thermo-junction, set into the drilled hole of the sample. For the measurement of conductivity the potentiometer was used and the current of 1mA flowed in the sample. By this method the results were obtained reversibly in the case of the raise and the fall of temperature. We see $FeO \cdot Fe_2O_3$ has much higher conductivity than Fe_2O_3. Thus, the dependence of conductivity on temperature shows relatively accurate value, although the sample may be a solid solution of $FeO \cdot Fe_2O_3$ and a small amount of Fe_2O_3.

We assume, conductivity of magnetite satisfies the following formula, $\sigma = \sigma_0 e^{\frac{-\varepsilon}{kT}}$, where k is Boltzmann's constant and ε is activation energy. In Fig. 8 $\log\sigma$ is plotted against $\frac{1}{T}$ in the temperature range 50°C~150°C. Sample (a) is sintered at 5×10^{-3} mm Hg. at 300°C; sample (b) and (c) are similarly sintered at 900°C for two hours, and the former is at 5×10^{-3} mm Hg. and the latter at 6 mm Hg. in vacuum respectively. In this case, activation energy was obtained 0.2 e.V. in the case of sample (a), 0.15 e.V. in sample (b) and 0.07 e.V. in sample (c), respectively. Sample (d), the natural magnetite, has the activation energy of 0.059 e.V.. The ohm-value in this figure shows the resistance of each sample at 50°C. From this figure, we realize, the raise of activation energy exhibits the decrease of conductivity. Fig. 9 shows conductivity of the natural magnetite in the region of low temperature. We find the kink of conductivity at −150°C, which corresponds to magnetic transformation. Above the temperature at the kink, activation energy is 0.059 e.V., which is the same value with activation energy of the natural magnetite in Fig. 8 measured in the temperature range 50°~150°C. Below this temperature it changes to 0.15 e.V., which corresponds to the value of sample (b) in

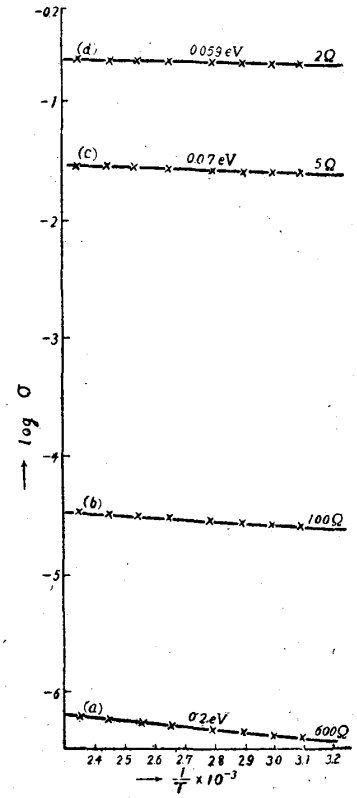


Fig. 8.

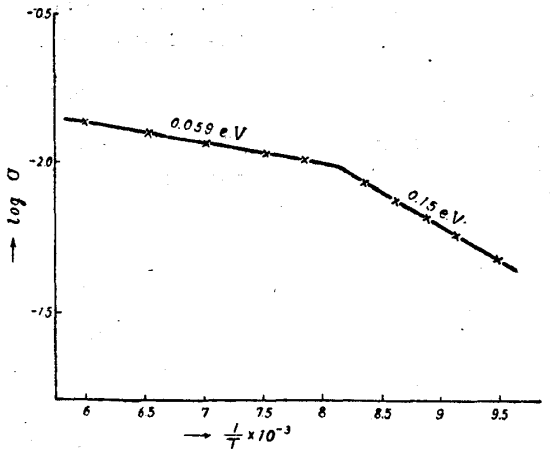
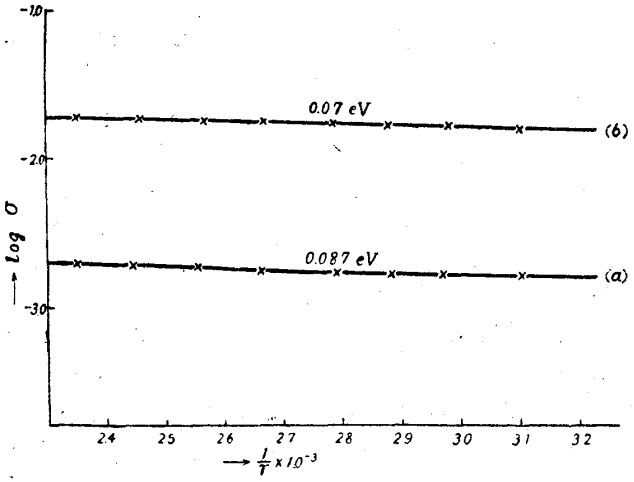


Fig. 9.

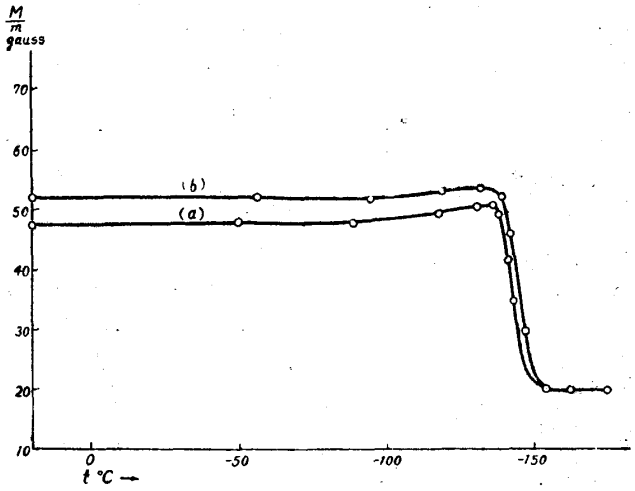
Fig. 8. These results show that conductivity of the artificial magnetite (c) in Fig. 8 has the kink which corresponds to magnetic transformation, and the magnetite (b) in Fig. 8. which does not exhibit magnetic transformation has not the kink. Sample (a) in Fig. 8, which contains H_2O in the crystal can not be estimated as perfect magnetite.

III. Properties of artificial Magnetite treated for various Time Durations of Heating



Fi.g 10.

Fig. 10 shows the observed value of conductivity in the temperature range 50°C~150°C. When the artificial magnetite obtained by wet method is treated at 6 mm Hg. pressure at 900°C for various heating time activation energy is 0.087 e.V. (a) for 30 minutes heating, 0.07 e.V. (b) for 2 hours heating respectively. Fig. 11 shows magnetic moment of the above artificial magnetite plotted against temperature in the region 0°C~−180°C, the ordinate represents magnetic moment per unit mass, the abscissa temperature; where magnetic transformation is observed. The curve (a) and (b) show the changes in magnetization of the samples due to temperature, which were heated for 30 minutes and 2 hours, respectively. By examining closely the results given in these figures, it is seen that the transformation always occurs at the same temperature −150°C.



Fi.g 11.

The decreasing value of the intensity of magnetization at the transformation point may be measured by the difference in comparison of activation energy in Fig. 10 with that of artificial magnetite 0.15 e.V., which has no magnetic transformation, but being considered that oxidation occurs to small extent by heat treatment and its composition deviates from magnetite, such a problem will be more complicated.

VI. Properties of the artificial Magnetite for various Temperatures of Heat Treatment

It is obvious from the experiments above mentioned, that the existence of magnetic transformation depends upon the vacuum degree, which oxygen atom can diffuse in the crystal of magnetite. In order to confirm the above fact in detail, we will attempt the experiment based on the following chemical reaction:

$$2(FeO \cdot Fe_2O_3)+\frac{1}{2}O_2 \rightleftarrows 3Fe_2O_3 .$$

In the air this reaction proceeds to right-hand side of this formula remarkably from

the neighbourhood of 150°C and magnetite is oxidized into γ-Fe_2O_3. Crystal form of γ-Fe_2O_3 is a spinel type indentical with that of magnetite and it shows ferromagnetic property, but its intensity of magnetization is lower than that of magnetite. γ-Fe_2O_3 is comparatively stable below 550°C. If the temperature is raised above 550°C, transition of crystal occurs and it changes to α-Fe_2O_3 which is paramagnetic. With increasing of temperature more and more, the reaction turns back to left-hand side of the above formula, i.e. the reduction of Fe_2O_3 begins, because $FeO \cdot Fe_2O_3$ is more stable than Fe_2O_3 at high temperature. Being considered that oxidation and reduction above remarked is a sort of diffusion of oxygen atom into the crystal, magnetite will tend to diffuse oxygen atom into the crystal at low temperature and release outwards from the crystal at high temperature on the contrary. So the artificial magnetite by heat treatment at 900°C at 5×10^{-3} mm Hg. in vacuum degree, which has no magnetic transformation, may diffuse oxygen atom into the crystal and exhibit magnetic transformation, when it is heated at lower temperature than 900°C, even if vacuum degree remains the same, 5×10^{-3} mm Hg.

Fig. 12 shows the changes in conductivity due to temperature in the range of 50°~150°C, of the various artificial magnetites obtained by wet method, which were heated at 5×10^{-3} mm Hg. in vacuum degree at 600°C, 700°C, 800°C, 900°C, and 1000°C respectively. Samples (a) and (b), the former treated at 600°C, the latter at 700°C, both containing H_2O in the crystal, they will not considered as perfect magnetite. Samples (c) ann (d) are heated at 800°C for one hour and two hours respectively, each having activation energy of 0.085 e.V. in (c) and 0.076 e.V. in (d). These results show, diffusion of oxygen atom into the crystal is possible and magnetic transformation can be expected, although vacuum degree is 5×10^{-3} mm Hg. Samples (e) and (f), the former treated at 900°C, the latter at 1000°C, have the same activation energy, 0.15 e.V.. They show no magnetic transformation. The ohm-value in this figure shows the resistance of each sample at 50°C.

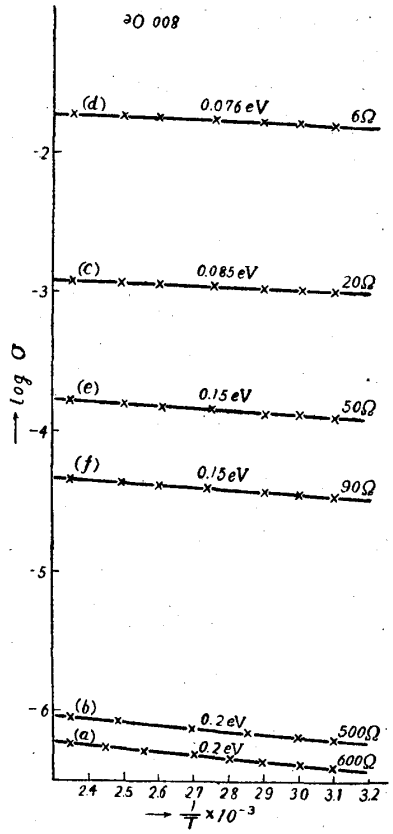


Fig. 12.

Summary

The results of the present investigation may be summarised as follows:-

We have ascertained, that in the artificial magnetite, the existence of magnetic transformation and break point of conductivity occurring when log σ is plotted against $\frac{1}{T}$ are due to an excess of oxygen in the crystal. Moreover, the intensity of magnetization and conductivity increase with the concentration of oxygen in the crystal, may have been shown. Having concern about the diffusion of oxygen in the crystal, crystal of $FeO \cdot Fe_2O_3$ will have perhaps vacant lattice point, for the ionic radius of oxygen is so large that oxygen atom can very seldom settle down interstitially into the lattice of $FeO \cdot Fe_2O_3$.

Comparing the conductivity of $FeO \cdot Fe_2O_3$ with that of other semiconductors, it is similar to Cu_2O that the various values of activation energy can be expected with the increasing of oxygen concentration. We know, Cu_2O is a defect semiconductor, the current being carried by positive holes. In

the case of $FeO \cdot Fe_2O_3$, owing to the oxygen rich lattice,$(3d)^{10}$ band of Fe^{++} or Fe^{+++} ion loses electrons and forms the positive holes if Fe^{++} and Fe^{+++} ions have higher energy than oxygen ions. The variation of activation energy and the existence of magnetic transformation will be illustrated if we assume the impurity level.

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